Title: Experimental determination of magnesiaum and silica solubilities in graphite-saturated and redox-buffered high-pressure COH fluids in equilibrium with forsterite + enstatite and magnesite + enstatite

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Abstract

We experimentally investigated the dissolution of forsterite, enstatite and magnesite in graphite-saturated COH fluids synthesized using a rocking piston cylinder apparatus at pressures from 1.0 to 2.1 GPa and temperatures from 700 to 1200 °C. Synthetic forsterite, enstatite, and ~~natural~~ nearly pure natural magnesite were used as starting materials. Redox conditions were buffered by Ni–NiO–H_2O, employing a double-capsule setting. Fluids, binary H_2O–CO_2 mixtures at the *P*, *T*, fO_2 conditions investigated, were generated from graphite, oxalic acid anhydrous ($H_2C_2O_4$) and water. Their dissolved solute loads were analyzed through an improved version of the cryogenic technique, which takes into account the complexities associated with the presence of CO_2-bearing fluids~~Redox conditions were buffered by Ni–NiO–H_2O, employing a double-capsule setting. Carbon saturated COH fluids were generated from~~

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~~graphite, oxalic acid anhydrous ($H_2C_2O_4$) and water (doped with 580 ppm of Cs). A diamond powder layer was employed to trap fluids with their dissolved solute loads, which were analyzed via cryogenic laser ablation ICP-MS.~~

The experimental data show that forsterite + enstatite solubility in H_2O–CO_2 fluids ~~results~~ is~~n~~ higher compared to pure water both in terms of dissolved silica ~~SiO_2 solubility values~~ ($m$$SiO_2$ = 1.24 mol/kg_{H2O} vs. $m$$SiO_2$ = 0.22 mol/kg_{H2O} at P = 1 GPa, T = 800 °C) ~~compared to the solubility in pure H_2O ($m$$SiO_2$ = 0.22 mol/kg_{H2O} at P = 1 GPa, T = 800 °C). Moreover, the presence of CO_2 also promotes the formation of Mg-solutes~~and magnesia (mMgO = 1.08 mol/kg_{H2O} vs. mMgO = 0.28 mol/kg_{H2O}~~at P = 1 GPa, T = 800 °C), at levels much higher than in C-free systems (mMgO = 0.28 mol/kg_{H2O} at P = 1 GPa, T = 800 °C)~~ probably due to the formation of organic C-, Mg- and Si-bearing complexes. C~~e~~ompared to forsterite + enstatite dissolution, m~~M~~agnesite dissolution in H_2O~~+~~ CO_2 fluids results in lower ~~MgO~~ magnesia solubility values~~contents~~ ~~compared to forsterite dissolution~~ (mMgO = 0.41 mol/kg_{H2O} at P = 1.5 GPa, T =800 °C) and ~~its behavior~~molalities that strongly resemble~~s~~ those associated with calcite solubility in pure water~~H_2O in terms of dissolved cations~~.

Our experimental results show that at low temperature conditions a graphite saturated H_2O–CO_2 fluid interacting with a simplified model mantle composition can lead to the formation of significant amounts of enstatite, while at higher temperatures, this fluid seems to be less effective in metasomatize the surrounding forsterite. COH fluids could represent an effective carrier of C-, Mg- and Si-bearing species from the mantle wedge to shallowest level in the upper mantle.

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1. Introduction

High-pressure aqueous fluids are able to transport significant amounts of dissolved species (Manning 1994) derived from interaction with rock-forming minerals. Experimental constraints on the extent of mineral dissolution are therefore crucial to understand metasomatic processes closely related to the mass transport of elements by high-pressure fluids. For example, quartz dissolution in H_2O at pressures and temperatures ranging from 0.1 to 2.0 GPa and 500 to 900 °C shows an increase of the total dissolved silica ($SiO_{2,aq}$) in H_2O with increasing P and T (Anderson and Burnham 1965; Manning 1994). The amount of solutes deriving from the dissolution of mantle minerals such as forsterite and enstatite ~~mobilized by~~in high-pressure fluids has been also extensively investigated in ~~H_2O only~~ systems

containing ~~only~~pure water as volatile component (Nakamura and Kushiro 1974; Ryabchikov et al. 1982; Manning and Boettcher 1994; Zhang and Frantz 2000; Newton and Manning 2002). Experimental evidence indicated that lower amounts of dissolved silica ~~solutes~~ results ~~in~~ from the dissolution of Mg-silicates (forsterite, enstatite)~~bearing systems compared to~~than ~~in the SiO_2–H_2O system~~compared to the dissolution of quartz.

~~For fluids bearing volatile carbon species in addition to water, several authors~~In the system SiO_2–H_2O–CO_2, mixed fluids show ~~(e.g., Newton and Manning 2000) investigated the dissolution of quartz in H_2O–CO_2 fluids showing~~ decreasing amounts of $SiO_{2,aq}$ with increasing content of CO_2 in the fluid (e.g., Newton and Manning 2000). However, the effect of CO_2 addition to aqueous fluids in equilibrium with mantle minerals has remained experimentally unexplored, ~~particularly under more reducing conditions in equilibrium with graphite,~~ even though carbon dioxide is thought to be a significant volatile species in subduction-related ~~subduction-related~~ fluids occurring in the slab–mantle interface (Tumiati et al., 2017).

1.1 Forsterite and enstatite solubility in H_2O

In early studies of silicate solubilities in aqueous fluids in the MgO–SiO_2–MgO (MSH) system at deep crustal and upper mantle conditions (P < 2 GPa and T < 1300°C), the composition of the fluid phase ~~was~~has been ~~derive~~estimated~~d~~ from phase relations projected to the H_2O–SiO_2 subsystem, assuming that the amount of MgO in the fluid was negligible at the investigated condition (Nakamura and Kushiro 1974; Ryabchikov et al. 1982; Zhang and Frantz 2000). ~~At deep crustal and upper mantle conditions (P < 2 GPa and T < 1300°C) the solubility of forsterite and enstatite in H_2O was investigated first by Nakamura and Kushiro (1974),~~ At 1.5 GPa and temperatures from 1280 to 1340 °C ~~who retrieved the composition of the fluid phase at P = 1.5 GPa and T = 1280–1340 °C from the location of phase boundaries in the system MgO–SiO_2–H_2O (MSH) and projected to the H_2O–SiO_2 subsystem axis, assuming that MgO concentration in the fluid was negligible at the investigated condition. The authors observed that an~~ aqueous fluids ~~in equilibrium~~saturated with forsterite and enstatite ~~was~~ are able to dissolve ~~a~~ significant amounts of SiO_2 ranging from ~~the~~ 18 wt.% at 1280 °C to ~~the~~ 22 wt.% at 1310 °C (Nakamura and Kushiro 1974). At 3 GPa and 1000 °C the Mg/Si ratio increases with pressure and

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reaches unity at 3 GPa and 1000 °C in a fluid containing > 30 wt.% ~~of silicate solutes~~dissolved silica (Ryabchikov et al. 1982).~~.~~

~~Ryabchikov et al. (1982) and Zhang and Frantz (2000) extended the *PT* range of the study of Nakamura and Kushiro (1974) to 3 GPa and 1 to 2 GPa respectively, and lower temperatures (*T* = 900–1200 °C) using the same technique to estimate fluid composition. Ryabchikov et al. (1982) observed that in the MSH system, the Mg/Si ratio slightly increases with pressure, reaching 1 at 3 GPa and 1000 °C, where the fluid contains more than the 30 wt.% of silicates. Moreover, Zhang and Frantz (2000), highlighted that the thermodynamic properties of aqueous silica derived from silica-saturated systems may not be applicable to calculation in silica-deficient systems at high-pressure conditions, due to the formation of silica dimers.~~

A~~nother approach to quantify the amount of solutes was to extract both fluids and precipitates from piston-cylinder experiments (Manning and Boettcher 1994). ~~. different experimental approach was used by Manning and Boettcher (1994), who developed a device to extract both fluids and precipitates from piston-cylinder experiments. The solution was then~~ analyzing them~~ed~~ by means of inductively coupled plasma ~~(ICP)~~ mass spectrometry (ICP-MS). Experimental data showed that at ~~the investigated conditions (~~*P* = 1–3 GPa and *T* = 700–1310 °C~~)~~ the concentration of MgO in the solution was negligible (< 0.005 mol/kg_{H2O}~~200 ppm~~) compared to ~~the~~ SiO_2 ~~content in the aqueous fluid~~ (*m*SiO_2 = 0.071 mol/kg_{H2O} at *P* = 1 GPa and *T* = 700 °C).

~~Subsequently~~With a third approach, ~~Newton and Manning (2002) applied~~ the weight loss technique (Newton and Manning 2002), ~~to measure the~~ solubilities~~y~~ of forsterite + enstatite were measured from 0.4 to 1.5 GPa and ~~*from*~~ *T* = 700–900 °C. Silica concentrations at 1 GPa increase from 0.16 mol/kg_{H2O} at 700 °C to 0.5 mol/kg_{H2O} at 900 °C, showing a small increase with pressure between 0.7 and 1.4 GPa. The higher solubility data compared to those of Zhang and Frantz (2000) (0.34 mol/kg at 1 GPa and 900 °C) were attributed by Newton and Manning (2002) to the quenching method employed by Zhang and Frantz (2000). It was suggested that decreasing temperature at nearly constant pressure could lead to the formation of hydrothermal enstatite, as the *P, T* path during quenching passed through the stability field of enstatite. The presence of enstatite having formed upon quench could have caused a misinterpretation of phase equilibrium boundaries by Zhang and Frantz (2000) leading to slightly underestimation of the silica content of the fluid.

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Finally,S Kawamoto et al. (2004a) employed an externally heated diamond anvil cell (DAC) and synchrotron X-ray fluorescence spectroscopy (S-XRF), coupled with an externally heated diamond anvil cell (DAC), was employed to investigate enstatite and forsterite solubility in aqueous fluids from 0.5 to 5.8 GPa and 800–1000 °C (Kawamoto et al. 2004a). At 3 GPa and 1000 °C it was observed that the authors observed that the Mg/Si ratio changes rapidly from SiO_2-rich to MgO-rich fluid, attributing this effect toprobably due to possible structural changes in liquid water (Kawamoto et al. 2004b).

Dissolution of solids in aqueous fluids generally increases with increasing *P*At higher pressure conditions, the diamond trap technique (Baker and Stolper 1994; Ryabchikov et al. 1989) has been employed to trap precipitates and melt in a diamond-powder layer placed in the experimental capsule and subsequently analyzed via LA-laser ablation ICP-MS (LA-ICP-MS). For example, at 6 to 10.5 GPa and temperatures from 900 to 1200 °C in the MSH system, Stalder et al. (2001) employed a diamond powder layer in the experimental capsule (Baker and Stolper 1994) to trap precipitates and melt that are subsequently measured via LA-ICP-MS. Melekhova et al. (2007) Employing this technique determined the MSH system was investigated from 6 to 10.5 GPa and temperatures from 900 to 1200 °C (Stalder et al. 2001) and the second critical endpoint was located in the MSH system to be above 11 GPa (Melekhova et al. (2007) employing an improved version of the diamond trap technique, where the diamond layer is kept frozen during the LA-ICP-MS analyses, below which minerals coexist with an aqueous fluid below the system's water-saturated solidus, and the total dissolved fluid load was determined by cryogenic LA-ICP-MS (freezing technique; (Kessel et al. 2004; 2005a; 2005b). Using the same technique, also known as the freezing technique, (Kessel et al. (2005a; Kessel et al. 2005b) quantified the total dissolved load of the aqueous fluid across the second critical endpoint in the potassium-free basalt – H_2O system from 4–6 GPa.

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1.2 Carbonate solubility in H_2O

Carbonate dissolution in H_2O has been investigated experimentally by several authors (Walther and Long 1986; Fein and Walther 1989; Caciagli and Manning 2003; Sanchez-Valle et al. 2003). The weight loss technique (Manning 1994) was employed to Caciagli and Manning (2003) investigated the dissolution of calcite in pure H_2O water up to P = 1.6 GPa and T = 500–900 °C (Caciagli and Manning 2003) through the weight loss technique (Manning 1994) extending the pressure range of previous calcite

solubility studies (e.g., Fein and Walther 1989). Results indicate that the solubility of calcite at 1 GPa increases with increasing temperature from 0.016 mol/kg at 500 °C to 0.057 mol/kg to 750 °C.

~~The first experimental dataset on carbonate solubility a~~At pressure ~~greater that 2.0 GPa~~ up to 3.6 GPa and low temperature conditions (T = 250 °C) ~~(Sanchez-Valle et al. 2003) investigated~~ strontianite dissolution in H_2O was retrieved employing an externally heated DAC and synchrotron X-ray fluorescence spectroscopy ~~up to 3.6 GPa and 250 °C~~(Sanchez-Valle et al. 2003)~~., employing an externally heated DAC and S-XRF.~~

~~In addition, a~~A significant effort has been made to develop thermodynamic models to predict carbonate behavior in aqueous fluids (Dolejs and Manning 2010; Pan et al. 2013; Facq et al. 2014; Pan and Galli 2016). ~~Facq et al. (2014) presented an integrated experimental and theoretical study of aragonite solubility in an aqueous fluid from 0.5 to 8 GPa and 300 to 400 °C.~~ Results indicate that HCO_3^- is the dominant species ~~from aragonite dissolution~~ in ~~an~~ aqueous fluids dissolving aragonite below 4 GPa and low temperature conditions (300–400 °C), while at higher pressures CO_3^{2-} becomes the dominant species, in contrast ~~with~~ to the previously hypothesized predominance of $CO_{2,aq}$ in aqueous fluids (Facq et al.~~(2014)~~. Moreover, accordingly to theoretical calculations, ~~Pan et al. (2013) predicted the solubility of different carbonate minerals, showing that~~ magnesite, insoluble in water at ambient condition, becomes ~~slightly~~ soluble at 10 GPa (Pan et al. 2013).

1.3 Solubilities in ~~COH~~ mixed H_2O–CO_2 fluids

~~So far, the amount of solutes mobilized by high-pressure fluids has been mainly investigated in CO_2-free aqueous systems even though CO_2 is considered a significant volatile in subduction-related fluids. In particular, the effect of CO_2 addition to aqueous fluids in equilibrium with mantle minerals remains experimentally unexplored.~~ Experimental data on mineral dissolution in mixed H_2O–CO_2 fluid are available only for quartz (Walther and Orville 1983; Newton and Manning 2000; Shmulovich et al. 2006; Newton and Manning 2009), albite and diopside (Shmulovich et al. 2001) and suggests that the presence of CO_2 lowers the solute content in the fluid by lowering the ~~silica~~ water activity (i.e., by increasing the CO_2 content).

To analyze the solubility of quartz in CO_2–H_2O mixed fluids, ~~–~~Walther and Orville (1983) developed an extraction quench-hydrothermal apparatus ~~to analyze the solubility of quartz in extracted~~

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~~CO_2–H_2O mixed fluids~~. In these experiments, performed in cold seal vessels, the pressure was limited to 0.2 GPa at T < 600 °C. ~~The authors observed a~~Results show a decrease in quartz solubility ~~by~~ with increasing ~~the~~ amounts of CO_2 in the ~~COH~~ fluid.

~~Concerning P–T conditions similar to our experimental study,~~ Another option is to ~~The collected solutes~~ extract and collect the solutes~~ed~~ from ~~the capsule~~piston cylinder experiments. Solutes ~~were mixed~~ with $LiBO_2$ and fused in graphite capsule at T = 1000 °C for 10 minutes (Schneider and Eggler 1986). ~~WDS analyses~~Glasses were then analyzed ~~performed employing~~using ~~the~~an electron microprobe. T~~Schneider and Eggler (1986) investigated t~~he solubility of different types of peridotites (amphibole-, phlogopite- and clinopyroxene-bearing~~jadeite~~ peridotites) and single minerals in mixed H_2O–CO_2 fluids were retrieved at P = 1.5–2 GPa and T = 600–1100 °C. ~~The collected solutes extracted from the capsule were mixed with $LiBO_2$ and fused in graphite capsule at T = 1000 °C for 10 minutes. WDS analyses were performed employing the electron probe.~~ ~~The authors observed~~Results show that the addition of CO_2 (9 mol%) to the aqueous fluid strongly ~~depressed~~ depresses the solubility of silicates by approximately one order of magnitude.

A modified version of the weight loss technique was employed to ~~Aranovich and Newton (1999)~~ determine~~d~~ activity-composition relations in CO_2–H_2O solutions (Aranovich and Newton 1999)~~by modifying the weight loss technique~~. The capsule was frozen in liquid nitrogen and punctured with a needle while still frozen. The immediate weight loss wa~~i~~s ascribed to CO_2 escape. The capsules were then dried and reweighed to retrieve the H_2O content. This technique, applied on double capsules, ~~that~~ was also ~~considered~~ used ~~later by Newton and Manning (2000; 2009), tw~~ho investigated quartz dissolution in H_2O–CO_2 at P = 0.2–1.5 GPa and T = 500–900 °C (Newton and Manning 2000; 2009)~~using the puncture-weight loss technique applied on double capsules~~. The ~~amount of~~solubility of SiO_2 in the fluid decreases strongly with increasing CO_2, in agreement with previous experimental data.

2. Experimental

2.1 Starting materials

Carbon-saturated ~~COH~~ H_2O–CO_2 fluids were generated starting from oxalic acid anhydrous (OAA; $H_2C_2O_4$), ~~H_2O~~ water and glassy carbon spherical powder (grain size 80–200 μm). The thermal dissociation of OAA ~~at T > 600 °C~~ generates a CO_2–H_2 fluid according to reaction:

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$$H_2C_2O_4 = 2CO_2 + H_2 \quad (1)$$

~~As an internal standard for LA-ICP-MS data quantification (Kessel et al. 2004), the H_2O was doped with 585 µg/g of cesium [$Cs(OH)_2$] and the Cs concentration was checked by means of ICP-MS. The addition of a~~A known amount of ~~Cs-doped H_2O~~water, added to ~~in~~ the capsule through a microsyringe, allowed~~s~~ to obtain a roughly equimolar CO_2–H_2O starting ~~mixture~~ fluid phase with XCO_2 [=CO_2/(H_2O + CO_2)] = 0.5. As an internal standard for LA-ICP-MS data quantification (see Kessel et al. 2004), ~~the H_2O~~water was doped with 585 µg/g of cesium [$Cs(OH)_2$]~~ and the Cs concentration was checked by liquid mode ICP-MS~~

Two ~~mineral assemblages~~different starting materials were considered: (i) a mixture of forsterite and minor enstatite (FoEn) and (ii) a mixture of enstatite, magnesite and minor forsterite (EnMgs). Forsterite and enstatite were synthesized from dried nano-crystalline $Mg(OH)_2$ (Sigma-Aldrich, 99.9% purity) and silicon dioxide (Balzers, 99.9% purity), mixed in stoichiometric proportions, pelletized and loaded in a vertical furnace at 1500 °C for 24 h. Synthesis products were ground in ethanol for 1 hour, dried and characterized by X-ray powder diffraction analysis (Bruker, AXS D8 Advance, ETH Zurich; Philips X'pert MPD, University of Milan). Natural magnesite from Pinerolo (Italy), checked for ~~im~~purity ~~and characterized~~ through electron microscopy and microprobe analyses (Jeol 8200 Superprobe, University of Milan), was ground under ethanol for 1 h and dried. The resulting composition of the mixtures, derived by Rietveld analysis, are: (i) forsterite 83.2 wt.%, enstatite 16.7 wt.% and cristobalite 0.1 wt.% for the starting material identified as FoEn, and (ii) magnesite 44.2 wt.% enstatite 39 wt.% forsterite 15.3 wt.% and cristobalite 1.5 wt.%, for the starting material EnMgs.

To collect fluids and solutes a layer of diamond crystals with grain size of 20 µm was placed between two layers of the starting mineral assemblages (FoEn or EnMgs). All experimental runs were performed at fluid-saturated conditions, with total fluids accounting for ~20 wt.%. An additional experimental run was performed at P = 1 GPa and T = 800 °C employing the starting material FoEn and a single Au capsule to measure the solubility of the assemblage forsterite + enstatite in pure water for comparison with previously published results (Newton and Manning 2002).

2.2 Experimental strategy

As the volatile composition of a graphite-saturated COH fluid is dependent on the redox state of the system, all the experimental runs were performed employing the double capsule technique (Eugster and Skippen 1967) and the nickel-nickel oxide (NNO) buffer to constrain the redox conditions.

The inner $Au_{50}Pd_{50}$ capsule was loaded with the starting materials, FoEn or EnMgs, OAA, ~~H_2O~~Cs-doped water, graphite and diamonds (Fig. 1). The outer capsule (Au at T < 1000 °C, Pt at T > 1000 °C) contained the inner capsule, ~~Ni, NiO~~NNO and H_2O. The NNO buffer fixes the chemical potential of H_2 (fH_2^{NNO}) in the H_2O-only fluid of the outer capsule. As long as the phases Ni, NiO and H_2O are present the fugacity of H_2 is fixed by the reaction:

$$Ni + H_2O = NiO + H_2 \quad (2)$$

The $Au_{50}Pd_{50}$ alloy of the inner capsule is permeable to hydrogen, therefore the chemical potential of H_2 is expected to be homogeneous in the inner and in the outer capsules. Since the inner capsule will contain in general a fluid with other COH species (such as CO_2) in addition to H_2O, the oxygen chemical potential in the inner capsule will be lower (Luth 1989) and can be calculated by thermodynamic modeling along with the volatile composition of the graphite saturated COH fluid.

The fugacities of oxygen (fO_2^{NNO}) and hydrogen (fH_2^{NNO}) fixed in the outer capsule by NNO were calculated employing the software package Perple_X (Connolly 1990; http://www.perplex.ethz.ch/) and the thermodynamic dataset of Holland and Powell (1998) ~~revised by these authors in 2004~~. The routines "vertex" and "fluids" were used first to calculate the fugacity of hydrogen fixed in the outer capsule by NNO + H_2O (Perple_X equation of state no. 16; H–O HSMRK/MRK hybrid EoS). Then, we calculated the speciation of the COH fluid through the Excel spreadsheet GFluid (Zhang and Duan 2010) with the EoS of Zhang and Duan (2009) and a modified H_2 fugacity coefficient (γH_2) changing dynamically as a function of X(O), fitted from the EoS of Connolly and Cesare (1993). This model has been proved to reproduce the composition of COH fluids in the pure C–O–H system (Tumiati et al. ~~in review~~2017). By assuming that fH_2 of the COH fluid in the inner capsule is equal to fH_2^{NNO}, we were able to calculate the molar fractions of volatiles (H_2O, CO_2, CO, CH_4, H_2 and O_2) at the investigated pressure and temperature conditions. The predicted fluids are mainly composed of H_2O and CO_2, with XCO_2 ratios changing as a function of pressure and temperature (Table 1).

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At T > 700 °C, the COH volatile composition is enriched in CO_2 compared to the starting equimolar H_2O–CO_2 composition given by OAA and H_2O. Equilibration of the COH fluid is accomplished by these coupled reactions:

$$H_2O \rightleftarrows H_2 + ½O_2 \quad (3)$$

$$C + 2O \rightleftarrows CO_2 \quad (4)$$

which can be condensed to the following water- (and graphite-) consuming reaction:

$$C + 2H_2O \rightleftarrows CO_2 + 2H_2 \quad (5)$$

The equilibration of the COH fluid at the experimental conditions implies that CO_2 is produced in the inner capsule by oxidation of graphite, a process that requires oxygen, which is taken from the dissociation of water. As a consequence, not only the XH_2O [=H_2O/(H_2O + CO_2)] of the COH fluid, but also the absolute quantity of water decreases in the inner capsule until equilibrium is reached at the experimental P and T conditions.

A P–T pseudosection for the system MS + COH at fO_2^{NNO} conditions was compiled employing the software Perple_X (Connolly 1990). As the composition of the COH fluid is constrained by the oxygen fugacity conditions, ~~but is~~ variable in the P–T field, the fO_2^{NNO}~~fO_2~~ conditions retrieved by thermodynamic modelling were fitted in equation:

$$\ln fO_2 = 10.75 + (-50077 + 0.32196\,P) / T \quad (6)$$

(P in bar and T in K), ~~which account for the variations in~~and the COH fluid composition in the P–T field is calculated accordingly. By fixing fO_2^{NNO}, t~~T~~he two resulting univariants (black solid lines in Fig. 2) are given by the reactions:

$$\text{forsterite + COH fluid } (fO_2^{NNO}) = \text{enstatite + magnesite} \quad (7)$$

and

$$\text{enstatite + COH fluid } (fO_2^{NNO}) = \text{talc + magnesite} \quad (8)$$

On the basis of the predicted stable assemblage in the P–T field we select as starting materials either FoEn or EnMgs (see Supplementary Material).

2.3 Experimental conditions

Experiments were carried out in a rocking piston-cylinder apparatus at pressures from 1.0 to 2.1 GPa and temperatures from 700 to 1200 °C. A r~~R~~ocking piston-cylinder apparatus was employed to

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guarantee the homogeneity of the sample through a rotation of 180° ~~of the entire structure of the piston cylinder apparatus~~. The rotation induces Rayleigh-Taylor instabilities, forcing the fluid to migrate and promoting chemical homogenization (Schmidt and Ulmer 2004). During the heating ~~phase~~ stage, the piston-cylinder rotated continuously (one turn of 180° every 30 s), then the rotation ~~rate~~ interval was changed to ~~99~~ 100 seconds. Experiments were performed for an average run time of 48 h. Quench rates are variable from 25 °C/second to 40 °C/second ~~at higher temperature conditions (T > 1000 °C)~~. The assembly consists in NaCl, Pyrex, a graphite heater and graphite disks at the bottom. The capsule was embedded in MgO rods filled with MgO powder. After the experimental run the recovered capsules were cleaned with diamond router bites and rinsed in a diluted HCl solution for 5 hours to eliminate residues of MgO from the capsule.

3. Analytical technique

The solute content in the fluid was measured through the cryogenic laser-ablation ICP-MS (Aerts et al. 2010), a modified version of the ~~technique also known as the~~ "freezing technique" (Kessel et al. 2004), which was applied in this experimental study for the first time on double capsules bearing COH fluids. The recovered experimental capsule was mounted on a freezing stage representing the base of the laser ablation cell, consisting of a stack of two Peltier elements, surrounded by plastic to thermally insulate the elements from the atmosphere (Aerts et al. 2010). The capsule holder is inserted into a copper block in direct contact with the Peltier elements and cooled to T = -35 °C. Conventionally, ~~the~~ frozen single capsules ~~were~~ can be cut open by hand using a razor blade (Kessel et al. 2004; Aerts et al. 2010); ~~H~~however, this method was hardly possible (and thus poorly controlled) in the present case because of the toughness of ~~the Ni-bearing~~ double capsules. Consequently, ~~controlled~~ capsule cutting was ~~ensured via addition of~~performed using a mechanical cutting device onto the freezing stage (Fig. 3a). This device allows to expose a longitudinal cross-section of the capsule by fastening a screw that pushes a cutter blade mechanically guided through a copper vice holding the capsule (Fig. 3b) while all is kept at -35 °C in a ~~hood~~ box flushed with dry Ar. Once the capsule is opened, the device is removed from the freezing stage together with the upper part of the capsule holder. The upper half of the capsule is inspected with a binocular microscope to help locating the diamond trap, while the lower part, always kept frozen, is

covered by the ablation cell top (Fig. 3c) and transferred to the microscope stage for ~~laser ablation~~LA-ICP-MS measurements.

The analyses were performed using a 193 nm ArF GeoLas Pro excimer laser system coupled to an ELAN DRC-e quadrupole mass spectrometer at the University of Bern. We analyzed the diamond trap for ^{24}Mg, ^{25}Mg, ^{26}Mg, ^{29}Si, ^{62}Ni, ^{133}Cs, ^{195}Pt and ^{197}Au, using a 60 µm beam diameter, ~13 J/cm^2 laser fluence and 5 Hz repetition rate. For Mg, all three isotopes were recorded in order to constrain the effect of polyatomic gas interferences ($^{12}C^{12}C$, $^{12}C^{13}C$, $^{12}C^{14}N$) on the final results. At -35 °C set in the freezing stage the CO_2 fraction unmixed from the COH fluid upon quench is not frozen, thus accounting for the low coherence of the trap during laser ablation measurement (and resulting craters were not well defined). Data were acquired in blocks of up to ~10 individual sample analyses bracketed by three analysis of the standard NIST SRM610, placed in the ablation chamber with the sample. Background was taken for ~50 seconds and the sample signal, on the diamond trap or on the solid residue, was collected for ~20 seconds. LA-ICP-MS data reduction was performed employing the software Sills (Guillong et al. 2008; http://www.geopetro.ethz.ch/research/orefluids/software) and in-house spreadsheets to calculate solute concentrations employing rigorous limits of detection filtering (Pettke et al. 2012) for each element and each measurement individually.

The cryogenic LA-ICP-MS technique was originally developed to analyze the solute content ~~of~~ in systems containing only H_2O as ~~volatile~~fluid component ~~only fluids~~. Cesium, introduced in the starting materials, is employed as the~~an~~ internal standard for data quantification, because it is a highly incompatible element that ~~fractionates~~ partitions completely into the fluid with the given mineral assemblages. In our experiments, we introduced a known amount of water ~~solution~~ doped with 585 µg/g Cs [as $Cs(OH)_2$]. As the initial Cs/H_2O ratio ~~was~~ is fixed, once the Cs concentration in the fluid phase coexisting with minerals at run *P* and *T* is known, solute concentrations of the fluid can be calculated (Kessel et al. 2004). However, compared to experiments bearing aqueous fluids coexisting with anhydrous silicates, our double-capsule, COH-bearing experiments are more complex, because (i) there is one fluid phase at run conditions (mostly a H_2O + CO_2 mixed fluid, plus solutes), exsolving two fluid phases (liquid H_2O + solutes, and gaseous CO_2) at quench conditions (see Fig. 1) and (ii) the initial Cs/H_2O is not fixed in our experiments, because the water content in the runs is variable, depending on *P*, *T* and fO_2 conditions. In double capsule arrangements, H_2 is in fact a mobile component that can be added

or removed from the system through diffusion in and out of the inner capsule. These conditions imply that the LA-ICP-MS data on systems bearing COH fluids refer to the aqueous part of fluids only, assuming that no solutes escape with the carbonic gas species upon capsule opening. Moreover, the latter point implies the initial Cs concentration cannot be used as an internal standard, unless this value is corrected to the $X\mathrm{H_2O}$ in the fluid at run P and T. To retrieve the amount of solutes in terms of mol/$\mathrm{kg_{H2O}}$ a correction for the change in total water mass present in the capsule relative to initial water mass loaded into the capsule is thus required.

If $\mathrm{H_2O}$ is consumed during fluid re-equilibration at run conditions, Cs concentration in the residual water increases; if $\mathrm{H_2O}$ is produced, Cs concentration decreases. We estimated the corrected Cs concentration at run P and T using a model, which assumes that fluid equilibration at NNO hydrogen fugacity condition is governed only by $\mathrm{H_2}$ mobility and no hydration or carbonation reactions involving minerals occur in the capsule charge. As long as these two assumptions are valid, it is possible to estimate the amount of Cs in the inner capsule in the following way using ~~a classic dilution equation:~~

~~$$C_i\mathrm{Cs} * V_i\mathrm{H_2O} = C_f\mathrm{Cs} * V_f\mathrm{H_2O} \quad (9)$$~~

~~where C_iCs is the initial concentration of Cs in the aqueous solution loaded into the capsule (585 ppm) and C_fCs is the final concentration of Cs after fluid equilibration at $f\mathrm{H_2}^{\mathrm{NNO}}$ conditions. $V_i\mathrm{H_2O}$ and $V_f\mathrm{H_2O}$ are the initial and final volume of water.~~

~~The volume of water is proportional to the moles according to:~~

~~$$V\mathrm{H_2O} = n\mathrm{H_2O} * V_{mol}\mathrm{H_2O} \quad (10)$$~~

~~($V\mathrm{H_2O}$, volume of water; n, number of $\mathrm{H_2O}$ moles; $V_{mol}\mathrm{H_2O}$, molar volume of water).~~

~~Considering that at fixed pressure and temperature conditions the molar volume of water is constant we obtain~~ the following dilution equation:

$$C_i\mathrm{Cs} * n_i\mathrm{H_2O} = C_f\mathrm{Cs} * n_f\mathrm{H_2O} \quad (9~~11~~)$$

where C_iCs is the initial concentration of Cs in the aqueous solution loaded into the capsule (585 µg/g) and C_fCs is the final concentration of Cs after fluid equilibration at $f\mathrm{H_2}^{\mathrm{NNO}}$ conditions. $n_i\mathrm{H_2O}$ and $n_f\mathrm{H_2O}$ are the initial and final number of $\mathrm{H_2O}$ moles.

The final Cs concentration will be given by:

$$C_f\mathrm{Cs} = \frac{C_i\mathrm{Cs} * n_i\mathrm{H_2O}}{n_f\mathrm{H_2O}} \quad (10~~2~~)$$

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As $n_i H_2O$ is known, i.e. the initial amount of water charged into the capsule, Eqn. (102) can be solved as long as $n_j H_2O$ is constrained. Solute concentrations in the pure water fraction of the fluid at run P and T can thus be calculated. For one experimental run, performed at 1 GPa and 800 °C, the volatile speciation of the fluid was retrieved experimentally by employing the capsule-piercing QMS technique (Tiraboschi et al. 2016) instead of calculating the amount of H_2O and CO_2 through thermodynamic modeling. The volatile composition consists of CO_2 (84.2 wt.%) and H_2O (15.8 wt.%). Compared to the experimental model employed to quantify the internal standard, the experimental volatile speciation appears to be enriched in CO_2 (see Table 1). The discussion relative to the different volatile speciation is presented elsewhere (Tumiati et al. in review2017). However, since the experimental result shows that the amount of H_2O in the inner capsule could be more variable than expected, the solubility of silica and magnesiaum were also calculated by varying the amount of H_2O in the experiments (plus or minus the 50 wt.%; available as Supplementary Material). Varying the amount of water does not affect significantly the amount of solutes, which variations are dominated by the analytical error. Consequently, the volatile speciation derived from thermodynamic modeling was employed to retrieve the solubility for all the other experimental runs.

For the experimental runs performed in the stability field of magnesite, we employed the EnMgs starting material to minimize the amount of newly formed carbonates. X-ray maps of elements and Principal Component Analysis (PCA) were considered used to evaluate the relative abundances of solid phases in the experimental runs and estimate the amount of CO_2 consumed to form new magnesite crystals. In fact, the initial amount of water charged in the capsule ($n_i H_2O$) will readjust if part of the initial CO_2 is consumed to form carbonates, as the system is buffered at NNO oxygen fugacity conditions. To maintain the CO_2/H_2O ratio determined by the oxygen fugacity conditions the amount of H_2O has to decrease in the inner capsule. Consequently the experimental runs performed in the magnesite stability field required an additional Cs correction. Capsules were inspected at the electron microscope (JEOL 8200 Superprobe, University of Milan) for presence of quench the eventual presence of precipitate magnesites in the diamond layer. Then the capsules were embedded in epoxy and polished, in order to perform wavelength-dispersive X-ray spectroscopy (WDS) electron probe analyses and X-ray elemental maps.

4. Results

In Figure 23, the run products are displayed together with the experimental carbonation curve of forsterite, determined on the basis of textural observations. The XCO_2 of the fluid given is shown as gray shaded contours. At the P–T–fO_2 conditions investigated, , from low to high pressure, we first observed three mineral the assemblage: (i) forsterite + enstatite (fo + en) assemblage, then; (ii) talc + magnesite (tc + mgs); (iii) then enstatite + magnesite (en + mgs). The majority of the experimental runs that started with the FoEn mix gave the same run products of forsterite + enstatite after the quench, with the exception of two experimental runs: (i) 1.5 GPa and 900 °C and (ii) 2 GPa and 1200 °C. At 1.5 GPa and 900 °C we observed newly formed magnesite from the forsterite + enstatite assemblage (Fig. 4a). At 2 GPa and 1200 °C the experimental run presents a sponge-like texture consisting of SiO_2 (Fig. 4b) with small dispersed enstatite crystals. No forsterite crystals were identified at these conditions; however, it has to be noted that the capsule was severely damaged during the cutting procedure for LA analyses. The experimental runs performed employing the EnMgs starting material at low-T conditions yielded the assemblage enstatite + talc + residual magnesite, and forsterite coronas were observed surrounding magnesite crystals at 1.2 GPa and 800 °C (Fig. 4c).

The solubility results expressed as mol/kg_{H2O} are reported in Table 2, together with the total amounts of solutes in wt.% and the calculated Cs concentrations (in µg/-g^{-1}) prevailing at run conditions in the pure water. No solubility data were obtained above 2 GPa and 1100 °C and at 1.5 GPa and 1100 °C, as the diamond trap was not completely preserved at these conditions (Fig. 4b and 4d). Moreover, solubilities were not retrieved at 1.5 GPa and 700 °C and 1.2 GPa and 800 °C due to the lack of equilibrium between solid phases (i.e., magnesite in the talc + enstatite assemblage and forsterite coronas on magnesite relics). In all experimental runs the NNO buffer assemblage was preserved after the quench. Graphite was also preserved below 2 GPa and 1200 °C.

Concerning analytical errors, Kessel et al. (2004) determined an uncertainty in the amount of H_2O in the fluid, derived from Cs analysis, ranging from 0.7 to 2.5%, which was similar (or smaller) than the standard deviation of their data. In our case, for each experiment, we reported the standard deviation, as our values are higher compared to the maximum uncertainty (2.5%) determined by Kessel et al. (2004). However, if only one laser-ablation shot is available (experimental runs CZ6, CZ5 and CZ9) we consider a minimum analytical error corresponding to that given by Kessel et al. (2004).

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4.1 Forsterite + enstatite assemblage

The SiO_2 contents reported as weight percentage in the water fraction of the fluid equilibrated ~~in the aqueous fraction of the COH fluid deriving from the equilibration~~ with forsterite and enstatite (Table 2) increases with pressure and temperature from 0.85 ± 0.15 mol/kg_{H2O} at 1 GPa and 700 °C to 4.21 ± 0.04 mol/kg_{H2O} at 1 GPa and 1100 °C and 4.60 ± 0.37 mol/kg_{H2O} at 2 GPa and 1100 °C (Fig. 5a). The MgO content also rises with *T*, from 0.67 ± 0.06 mol/kg_{H2O} at 1 GPa and 700 °C to 6.90 ± 0.07 mol/kg_{H2O} at 1 GPa and 1100 °C; while from 1 to 2 GPa at 1100 °C we observe identical *m*MgO values within errors (6.90 ± 0.04 mol/kg_{H2O} at 1 GPa; 6.12 ± 0.99 mol/kg_{H2O} at 2 GPa) (Fig. 5b).

The solubility of forsterite + enstatite in COH fluids was compared with the solubility of the same assemblage in pure water, by performing a dissolution experiment at P = 1 GPa and T = 800 °C (white dots in Fig. 5a). At these conditions, SiO_2 dissolved in pure water (0.22 ± 0.06 mol/kg_{H2O}) is much lower than SiO_2 dissolved in the COH fluid (1.24 ± 0.19 mol/kg_{H2O}). In a similar way also the MgO content from forsterite and enstatite dissolution in the COH fluid is higher compared to dissolution in ~~the~~ H_2O ~~only system~~: from 0.28 ± 0.04 mol/kg_{H2O} in H_2O to 1.08 ± 0.10 mol/kg_{H2O} in the MS + COH system (Fig. 5b).

4.2 Enstatite + magnesite assemblage

Two experimental runs were performed above the forsterite carbonation reaction (see Fig. 3). For these experiments the amount of SiO_2 and MgO in the aqueous fraction of the COH fluid was retrieved considering that a part of the initial CO_2 in the inner capsule was consumed to produce carbonate~~s~~. The amount of SiO_2 at 1.5 GPa from 800 to 900 °C (Table 2) is similar within analytical error (0.41 ± 0.02 mol/kg_{H2O} at 800 °C; 0.53 ± 0.23 mol/kg_{H2O} at 900 °C; Fig. 5a), while the *m*MgO tends to increase with temperature from 0.47 ± 0.09 mol/kg_{H2O} at 800 °C to 0.73 ± 0.29 mol/kg_{H2O} (within the stated uncertainties; Fig. 5b). Compared to the forsterite + enstatite assemblage, the SiO_2 concentration in the fluid coexisting with enstatite + magnesite is significantly lower, suggesting a lower solubility of enstatite in the COH fluid compared to forsterite. The MgO content is slightly lower compared to the fluid in equilibrium with forsterite and~~+~~ enstatite ~~assemblage~~, however we also have to consider that the

pressure conditions are different (1.5 GPa for en + mgs; 1 GPa for fo + en) and the Mg could derive from either magnesite or enstatite, or from a combined effect.

5. Discussion

5.1 Comparison with previous solubility studies

In this experimental study, we provide for the first time solubility measurementss of forsterite, enstatite and magnesite dissolution in a mixed H_2O–CO_2 fluid in equilibrium with graphite. To validate our approach we also performed an experimental run in the system MgO–SiO_2–H_2O, to compare results of our analytical technique with those obtained in previous studies on mineral solubility. Our experimental data relative to the dissolved SiO_2 in an aqueous fluid coexisting with forsterite and enstatite at 1 GPa and 800 °C ($m$$SiO_2$ = 0.22 mol/$_{H2O}$kg) is within error identical within uncertainties withto the amount of SiO_2 determined by Newton and Manning (2002) ($m$$SiO_2$ = 0.21 mol/kg$_{H2O}$) considering similar starting materials and run time. Our experimental data fit quite well also with other literature data (Nakamura and Kushiro 1974; Manning and Boettcher 1994; Zhang and Frantz 2000; Newton and Manning 2002) on SiO_2 solubility in the same system (white dot in Fig. 6a, open symbols), considering the differences in starting materials and technique employedemonstrating that different experimental strategies yield to comparable resultsd.

Regarding theAs far as the amount of MgO dissolved in an aqueous fluid with forsterite and enstatite is concerned, there are to date no published experimental data available to date for the P–T conditions of 1 GPa and 800 °C investigated here. Extrapolation of MgO solubility derived from the dissolution of forsterite and enstatite in pure water from data obtained at P = 1–2 GPa and T = 900–1200 °C reported in Zhang and Frantz (2000) suggests a solubility below 0.17 mol/kg for our experimental conditions. Our measured fluid mMgO = 0.28 mol/kg$_{H2O}$ (Fig. 6b) is higher. However, because our value represents the first experimental direct measurement at moderately high-pressure of dissolved MgO in the MgO–SiO_2–H_2O system, this discrepancy cannot be evaluated further.

5.2 Dissolution of forsterite, magnesite and enstatite in COH fluids and comparisons with dissolution in H_2O only systems

Compared with the solubility in the $MgO–SiO_2–H_2O$ system, both the amounts of SiO_2 and MgO dissolved in the aqueous fraction of a COH fluid from forsterite + enstatite are higher (Fig. 6). This result suggests that, in contrast to what is observed for instance in the $SiO_2–H_2O–CO_2$ system (Newton and Manning 2000), in the MS-COH system the CO_2 component of the COH fluid does not act merely as an inert diluent, i.e. lowering the amount~~s~~ of solutes dissolved in the fluid. Instead, carbon dioxide seems to promote the dissolution of Mg-bearing silicates, favoring the formation of complexes involving Mg and C, as suggested by the higher MgO content in the aqueous fraction of COH fluid compared to the MgO dissolved in ~~a~~ H_2O ~~only fluid~~ at the same experimental conditions (P = 1 GPa and T = 800 °C). Similarly, as the amount of SiO_2 is also higher compared to dissolution in H_2O ~~only fluids~~, the results suggest the formation of complexes potentially involving Mg, C and Si, in addition to the solutes generated by the effect of the aqueous component of the fluid (e.g. silica monomers and dimers as suggested by ~~, following~~ Newton and Manning 2002). ~~However,~~ The presence of Si-C complexes has not previously detected in the system $SiO_2–H_2O–CO_2$, where the main dissolved species was though to be a neutral dihydrate of silica with one to three attached (solvated) H_2O molecules (Newton and Manning 2000). However, i~~t~~ should be noted that the ~~latter~~ cited experiments did not involve graphite.

There are two possible options to interpret the increase in dissolved SiO_2 in the MS–COH system: (i) the generation of Mg-Si-C complexes, and (ii) the production of a SiO_2 residue due to the formation of Mg-C solutes from forsterite and enstatite, which is highly soluble in H_2O (Manning 1994). In this experimental study, the dissolution process has been quantified in terms of absolute major element solubilities in the fluid, therefore information on the speciation can only be gained indirectly, through thermodynamic modeling (see Section 5.3). However, the formation of SiO_2 and Mg–C solutes has been directly observed in the experimental runs where the solubility data were not available (P > 2 GPa and T > 1100 °C), as the diamond trap was no longer preserved. In these runs the fluid was not completely ablated during LA-ICP-MS measurement, therefore it was possible to ~~visualise~~ characterize precipitates by backscattered electron (BSE) imaging of unpolished and polished samples. At 2.1 GPa and 1100 °C precipitates appear as SiO_2 droplets (Fig. 7a) and as vesiculated aggregate or acicular Mg–C solutes, probably hydrated (Fig 7b). WDS analyses show detectable Cs quantity (up to 0.07 wt.%), while for other solid phases Cs was below detection limit, confirming an origin as fluid quench precipitate. However, we note that in this experimental run, only few diamonds were retrieved. We suggest that diamond

dissolution could have occurred at the experimental conditions. In fact, Fedortchouk et al. (2007) observed that after 35 hours at P = 1 GPa and T = 1350 °C a diamond of 5 mm loses nearly 40 wt.% of its initial weight at NNO oxygen fH_2 conditions. Considering that the diamonds employed in our studies are significant smaller (20 μm) while the experimental pressure is higher (P = 2–2.1 GPa) dissolution seems to be the process most plausible for the lack of diamonds, at least at the highest temperature conditions.

At 2 GPa and 1200 °C forsterite, diamonds and graphite were completely dissolved in a silica-rich vesiculated glass with few enstatite crystals dispersed. The observed texture is extremely similar to an experimental run performed by Cruz and Manning (2015) in the SiO_2–H_2O–NaCl system at 1.5 GPa and 1100 °C. The authors suggested that a similar feature indicates the presence of two distinct fluids, one hydrous Si-rich fluid and the other saline and relatively Si poor. In our experimental runs the relatively Si poor fluid could be constituted by Mg–C complexes, as shown in Figure 7a. However, it remains unclear why in this experimental run the Mg-bearing fluid was not identified. Moreover, the presence of a miscibility gap seems unlikely in a NaCl-free system and could result simply from the quench process.

In Figure 8, solubilities of silica and magnesi~~um~~ are plotted versus the XCO$_2$ of the coexisting COH fluid. In both cases we observe an increase with temperature and XCO$_2$. On the other hand, the behavior of SiO_2 and MgO is different when it comes to increasing pressure: while the SiO_2 content slightly increase (Fig. 8a), MgO shows higher values at lower pressure and high temperature conditions (P = 1 GPa; T = 1100 °C), where the COH fluid is mainly composed by CO_2 (XCO$_2$ = 0.85) (Fig. 8b). At high temperature conditions CO_2 favors the formation of Mg–C complexes, while H_2O, present in significantly minor quantity, appear to dissolve less SiO_2. With increasing pressure the XCO$_2$ lowers, consequently the effect of CO_2 is weakening, while the aqueous component becomes more effective in dissolving the SiO_2 residue.

The amount of solutes derived from the dissolution ~~in a COH fluid~~ of the assemblage magnesite + enstatite in a COH fluid can be compared to the experimental data from Caciagli and Manning (2003) relative to simple calcite dissolution in H_2O. The dissolved cations in this case are Mg and Si instead of Ca, and the fluid composition is COH fluid instead of pure H_2O. Solute amounts for Mg and Ca are similar and in agreement with literature data (Fig. 9), suggesting similar solubilities for $CaCO_3$ and $MgCO_3$ at the PT conditions investigated here, irrespective of the more complex chemistry of our system. As thermodynamic models indicate that pure magnesite is slightly soluble in H_2O at 10 GPa (Pan et al.

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2013) and has a lower solubility compared to calcite over a significant pressure range (1 to 10 GPa)~~,~~. This comparison shows that either (i) the addition of CO_2 to an aqueous fluid enhances magnesite dissolution compared to ~~a~~ H_2O ~~only~~, or (ii) that solvation of Mg in our experimental system involves Mg-Si species, or both. Concerning possibility (i) we observe that our experimental amount of SiO_2 dissolved from enstatite is quite similar to that in ~~a~~ H_2O ~~only fluid~~ (0.41 mol_{SiO2}/kg_{H2O} in COH fluid at 1.5 GPa and~~/~~ 800 °C versus 0.42 mol_{SiO2}/kg_{H2O} at 1 GPa and 850 °C, Newton and Manning 2002). And our SiO_2 solubilities at 1.5 GPa and 900 °C (0.53 mol/kg_{H2O}) are similar to those obtained for pure water coexisting with enstatite + forsterite at 1.4 GPa and 900 °C (0.51–0.52 mol/kg_{H2O}; Newton and Manning 2002). SiO_2 dissolution thus seems to be governed by the H_2O component, and no positive or negative effect caused by CO_2 addition to the fluid can be discerned. Because the molalities of dissolved Si and Mg are equal within uncertainties, dissolution of a magnesite component is not indicated, which is consistent with the very low Mg solubility reported by Pan et al. (2013).

5.3 Theoretical solute speciation modeling

In order to ~~gain some insight into~~characterize the possible aqueous species relevant to ~~the~~ our experimental system ~~investigated~~, we employed a thermodynamic model that, in addition to neutral COH species, also takes into account Mg and Si-bearing dissolved species. We performed calculations using the aqueous speciation-solubility code EQ3 (Wolery 1992) adapted to include equilibrium constants calculated with the Deep Earth Water (DEW) model (Facq et al. 2014; Sverjensky et al. 2014). We focused on the solubility measurements at 800 °C and 1.0 GPa, as results were available for the solubility of Mg and Si in the MS-H system as well as the MS-COH system. The two sets of Mg and Si solubility data enabled characterization of a Mg-OH complex and a Mg-Si-C complex.

For the MSH system ~~MS-H~~, silica concentrations predicted using the silica monomer and dimer in the DEW model agreed, as expected, with the experimentally measured values. However, matching the experimental Mg concentration required an $Mg(OH)_2$ complex in addition to the predicted value for $Mg(OH)^+$. Trial and error regressions of the experimental data for the MS-H and the MS-COH systems indicated that $Mg(OH)^+$ could not account for the measured Mg concentrations in both systems. Instead, the data for the MS-H system was used to retrieve the equilibrium constant for the second $Mg(OH)_2$ complex given by the equilibrium

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$$Mg(OH)_2 + 2H^+ = Mg^{2+} + 2H_2O \quad (113)$$

as in Table 3.

In the system MS-COH, the model Mg-solubilities using the new Mg-OH complexes were still too low, indicating the likely need for additional Mg-bearing complex. Furthermore, the predicted Si-solubility based solely on the monomer and dimer was also way too low because it remained the same as for the C-free system (Table 3). Trial and error regressions using various species such as $MgHCO_3^+$, $MgCO_3$, $MgHSiO_3^+$, and $MgSiO_3$ failed to adequately describe the experimental data for the MS-COH system given what was already known about the stabilities of these complexes. Instead, the data for the MS-COH system was used to retrieve the equilibrium constant for a complex involving Mg, Si, and C according to the equilibrium

$$Mg[OSi(OH_3)][CH_3CH_2COO] + H^+ = Mg^{2+} + SiO_{2,aq} + CH_3CH_2COO^- + H_2O \quad (124)$$

as in Table 3. This complex, which involves carbon, results in the solubility of Mg and Si fO_2 dependent. Propionate involves reduced C. Therefore, calculated solubilities involving Eqn. (124) increase at lower fO_2 values and decrease at higher fO_2 values. Eqn. (124) is only important for reducing systems. It should not be significant at all in COH fluids from all previous studies of Mg-silicate solubilities or stabilities that have focused on oxidizing conditions without graphite. Consequently, Eqn. (124) provides an explanation for the distinctive enhanced solubilities of Mg and Si measured in the present study, which does involve graphite, and, presumably, aqueous species involving reduced carbon. Volatile reduced C-species have in fact been detected in chemical analyses of the volatiles dissolved in the MS-COH system with graphite (Tumiati et al. ~~in review~~2017), as well as implied by model calculations of the COH fluid compositions (Table 1).

A more complete analysis of the potential importance of Eqn. (124) over a wide range of temperatures and pressures is hampered by the lack of experimental Mg-solubility data in the MS-H system, which is needed for quantification of Eqn. (113). Consequently, a full equation of state characterization of the standard partial molal properties of the Mg-Si-C-complex must await the development of several estimation schemes for predicting the properties of the Mg-OH complex in Eqn. (113). This will be the subject of a future study.

5.4 Forsterite carbonation curve

Although the experiments performed were aimed to measure fluid composition and were not reversed, we reported in Fig. 2 the forsterite carbonation reaction. The reaction shows a weak pressure dependency and occurs at higher pressure compared to the one determined by Koziol and Newton (1998) in the MgO–SiO_2–CO_2 system. The shift toward higher pressures is predicted also by the calculated reaction through a thermodynamic model and is probably caused by the presence of H_2O in the investigated experimental system. With increasing temperatures and molar fraction of CO_2 the reaction approaches that of Koziol and Newton (1998) as the composition of the fluid becomes more CO_2 rich.

5.5. Implications for metasomatic processes

Several authors investigated the MSH system as a simplified model for melting and solubility in hydrated peridotites (e.g., Kushiro et al. 1968; Ryabchikov et al. 1982; Inoue 1994; Luth 1995; Zhang and Frantz 2000; Stalder et al. 2001; Mibe et al. 2002; Hack et al. 2007). Available experimental data on mineral solubility in the MSH system indicates that at low-pressure conditions (< 3 GPa) the amount of dissolved SiO_2 in the aqueous fluid is significantly higher compared to MgO (e.g., Zhang and Frantz 2000; Newton and Manning 2002). At these conditions, an aqueous fluid, migrating upward through the upper mantle, dissolves up to the 20 wt.% of silica, leaving a SiO_2-depleted mantle and a relatively SiO_2-enriched crust (Nakamura and Kushiro 1974). This process results in the formation of enstatite relative to forsterite, as the Mg/Si ratio is significantly lower than unity. However, the Mg/Si ratio derives from experimental data limited to SiO_2, as no measures of MgO solubility in aqueous fluid are available at low-pressure conditions. Our experimental study presents for the first time, the amount of both SiO_2 and MgO dissolved in an aqueous fluid in equilibrium with forsterite and enstatite (MSH system) and consequently provides the first experimentally based Mg/Si ratio. At 1 GPa and 800 °C the aqueous fluid shows a significantly higher Mg/Si ratio (= 1.27) than previously reported in literature.

In Figure 10 a ~~*thermodynamic model* *T*–*X*~~ isobaric pseudosection is presented to show the effect of variable Mg/Si ratios in ~~the~~ fluids reacting with ~~fa~~ forsterite~~-~~, being ~~-~~Mg/Si~~-~~ = 0 at X = 0, and Mg/Si~~-~~ = ~~1~~2 at X = 1. Assuming a complete reaction between 25 wt.% fluid and 75 wt.% forsterite, fluids with a Mg/Si ratios < 2 will modify the system bulk compositions, so that enstatite may form. In the MSH system the amount of enstatite produced by this fluid is approximately + 10 mol% (open symbol in Fig. 10). In the MS + COH system the Mg/Si ratio is lower compared to the MSH system (filled symbols in

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Fig. 10) and increases with temperature. At low-*T* conditions the amount of enstatite produced by the reaction would be higher (~ + 17 mol%) compared to high-*T* conditions, where the amount of orthopyroxene produced will be less than 5 mol%. The calculated amount of fluid, expressed as g_{H2O}/mol forsterite, to complete the reaction varies from 197 in the MS + COH system to 602 in the MSH system at 1 GPa and 800 °C. Therefore, in the MS + COH system lowers amounts of fluid are required to metasomatize the forsterite compared to the MSH system, where a significant higher quantity of water is needed. Moreover, with increasing temperature the amount of fluid employed to complete the reaction lowers, reaching 27 g_{H2O}/mol forsterite at 1 GPa and 1100 °C.

Our experimental data shows that at low temperature conditions a CO_2-bearing fluid could produce higher amount of enstatite compared to an aqueous fluid, while at high temperature conditions (*T* > 1000 °C) the fluid seems to be less effective in metasomatize the surrounding forsterite. In a mantle wedge flushed by H_2O and CO_2 in presence of graphite (Galvez et al. 2013), where subsolidus conditions prevail, the formation of enstatite would be favored compared to a system where the only volatile species is H_2O. On the other hand, higher temperature conditions will favor the migration of C-, Mg- and Si-bearing fluids to shallowest level in the upper mantle, as the fluid is less reactive with the surrounding forsterite.

6. Conclusions

In this experimental work we present the first measurements of dissolved SiO_2 and MgO in graphite-saturated COH fluids from two different assemblages, forsterite + enstatite and magnesite + enstatite. We employed the cryogenic LA-ICP-MS technique on double capsule assemblages to quantify SiO_2 and MgO solubility in the aqueous fraction of COH fluids buffered at Ni–NiO–H_2O. The presence of CO_2 increases the solubility of forsterite and enstatite compared to systems containing only H_2O ~~only~~ as volatile component~~fluid~~. Moreover, magnesite solubility in a COH fluid is similar to that of calcite in pure H_2O. Our results indicate that in a Mg-bearing system CO_2 does not act merely as an inert diluent, by lowering the solubility of solid phases. On the contrary, CO_2 favors the formation of Mg-Si-C complexes, leading to a graphite-saturated COH fluid containing significant amounts of dissolved reduced carbon species. Our experimental study highlights the importance of COH fluids in transporting Mg, Si, and C at subsolidus conditions. At high temperature conditions these fluids seem to interact

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poorly with the surrounding peridotite and could represent an effective way to mobilize C-bearing species to shallowest level in the mantle, along with diapirism of slab rocks (Marschall and Schumacher 2012; Tumiati et al. 2013) and melt generation (Poli 2015).

~~Overall~~From an analytical point of view, the cryogenic LA-ICP-MS technique, coupled with other techniques to characterize the volatile speciation of the fluid (e.g., Tiraboschi et al. 2016) represent a significant improvement towards a comprehensive characterization of fluids, in terms of volatile speciation and dissolved solute species.

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